

# Recent Fluctuations of Chlorobiphenyls (PCBs) in the Green Bay, Wisconsin, Region<sup>\*</sup>

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## Introduction

During the past six years, Wisconsin and Michigan have maintained a major stocking program for trout and salmon in Lake Michigan in an effort to re-establish a sport fisheries, and to control nuisance fish, such as the alewife. In 1969, Veith and Lee (1) found these large predators contained chlorobiphenyls (PCBs) at concentrations ranging from 10 to 25  $\mu\text{g/gm}$  (fresh weight—as Aroclor 1254). Furthermore, the coho salmon eggs contained 12 to 17  $\mu\text{g/gm}$  PCBs (fresh weight) which, based on the results of Johansson et al. (2) suggest that the PCBs may contribute to the poor reproductive success of the stocked fish in Lake Michigan. The seizure of fish from Lake Michigan, because of the presence of chlorinated pesticides and PCBs at concentrations greater than that regarded as safe for human consumption, has demonstrated that the continuous input of trace quantities of these chemicals may jeopardize major food resources for man, if proper management of hazardous chemicals is not practiced.

There are numerous examples of the aqueous transport of PCBs originating from industrial and sanitary wastes (3, 4). Veith and Lee (5) reported the presence of PCBs in sanitary wastes of all

cities and villages studied in the Milwaukee River (Wisconsin) watershed. Dube (6) has found similar results in a study of PCBs in municipal wastes from southeastern Wisconsin. All of these data were obtained prior to or shortly after the voluntary partial ban on PCB sales by Monsanto Company. This paper presents the preliminary data from studies of the levels and sources of PCBs in rivers discharging into Lake Michigan—Green Bay in northeastern Wisconsin.

Green Bay (Figure 1) is an 120-mile long elongated bay in the northwest corner of Lake Michigan. The major rivers tributary to lower Green Bay are the Fox (mean discharge of  $11 \times 10^6 \text{ m}^3 \text{ day}^{-1}$ ), which enters at the southwest end of the Bay, and the Oconto ( $2 \times 10^6 \text{ m}^3 \text{ day}^{-1}$ ), Peshtigo ( $2 \times 10^6 \text{ m}^3 \text{ day}^{-1}$ ) and the Menominee ( $9 \times 10^6 \text{ m}^3 \text{ day}^{-1}$ ), all of which enter along the northern shore of the Bay (7). The Fox and Menominee Rivers receive the wastes from the cities of Green Bay and Marinette (Wisconsin)—Menominee (Michigan), respectively. The Oconto River receives the wastes from Oconto Falls and Oconto, and wastes from the city of Peshtigo are discharged into the Peshtigo River. The Big Suamico and Pensaukee Rivers primarily drain agricultural and forested land and do not receive any major municipal wastes above the respective sampling sites.

## Experimental Procedures

### Field Sampling

The procedures used in this study have been discussed in detail elsewhere (5). The collection of water was conducted with all-glass systems to

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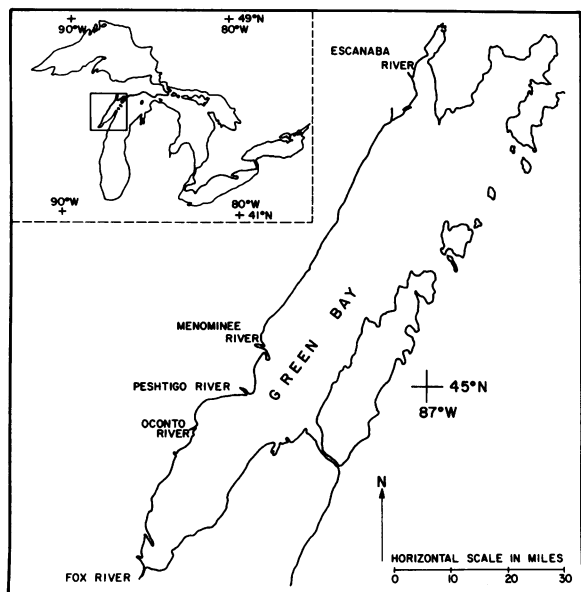


FIGURE 1. Location of Green Bay, Lake Michigan and major rivers tributary to the Bay.

preclude possible interaction of the sample with rubber, plastic, or polyvinyl chloride surfaces. Samples were collected from the river by submerging a weighted, glass carboy (20 l) at a depth of 0.2 m in the center of the main channel. Preservatives were not added, as samples were cooled and extracted within 24 hours of collection.

### Extraction

Water samples (20 l) were batch-extracted twice with hexane in 2 l separatory funnels. The hexane portions were combined, dried with anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated to 15 ml for cleanup in a gentle air stream.

### Liquid Chromatography

The cleanup of extracts for gas chromatographic analysis was conducted with liquid chromatography on Florisil, as described by Reynolds (8) and Hughes et al. (9). The media (Kensington Scientific) was extracted in a Soxhlet extractor for 24 hours with an azeotrope of hexane and acetone (1:59) to remove organic impurities. The azeotrope was evaporated from the Florisil at 105°C, and the Florisil was heated to 650°C for 2.5 hours for activation.

The Florisil column for preliminary cleanup was prepared by vibrating 19 g of Florisil into a 25 mm o.d. glass column, which was fitted with a glass frit and Teflon stopcock. The column was topped with 10 g anhydrous sodium sulfate to prevent deactivation of the Florisil by traces of water in the extract. The extracts were placed on the column and eluted with hexane (200 ml) to recover the PCBs, if present. With some samples, it was necessary to rechromatograph the hexane eluate from the 25 mm o.d. Florisil on a smaller diameter Florisil column (9 mm i.d.) to isolate the PCBs from organic interferences. If necessary, the PCBs were separated from the DDT group of pesticides through chromatography on silicic acid (10, 11).

### Instrumentation

The analyses of water extracts were conducted on an Aerograph 1745-20 gas chromatograph equipped with concentric tube electron capture detectors ( $^3\text{H}$ , 250 mC) and a 50:50 effluent splitter for simultaneous analysis with electron capture and flame ionization detectors. Analytical GLC columns consisted of 2.0 m  $\times$  1.8 mm glass coils which were packed with either OV-101 (3 percent), OV-101/XE-60 (3:3 percent), or OV-101/QF-1 (3:4.5 percent), coated onto Gas Chrom Q (720/140 mesh). The carrier gas (purified  $\text{N}_2$ ) was maintained at 21 ml  $\text{min}^{-1}$ ; and the injector, column, and detector temperatures were 250°C, 180°C, and 220°C, respectively.

### Analysis

The commercially prepared PCBs in the U.S.A. (Monsanto Company, St. Louis, Mo.) exist as seven complex mixtures under the name "Aroclor", which range in chlorine content from 21 to 62 percent. When the PCB mixtures are chromatographed with GLC, the mixtures of isomers produce both resolved and superimposed peaks and are somewhat characterized by the GLC fingerprint presented as relative peak heights and retention times. Because of the complexity of the mixtures, determinations have been quantitatively defined by comparing the area of a sample chromatogram to the area of a known quantity of the commercial mixture which most closely resemble that of the sample.

**Table 1. Variations of Chlorobiphenyls in Rivers in the Green Bay Study Area.**

| River                      | Concentration ( $\mu\text{g/l}$ as Aroclor 1254) <sup>a</sup> |         |           |           |
|----------------------------|---|---------|-----------|-----------|
|                            | 12/29/70  | 5/21/71 | 7/20/71   | 8/6/71    |
| Peshtigo River, Peshtigo   | 0.31  | 0.38    | <0.01     | <0.01     |
| Oconto River, Oconto       | 0.45 (3)  | 0.16    | <0.01     | <0.01 (3) |
| Pensaukee River, Pensaukee | <0.01   | <0.01   | <0.01 (1) | <0.01 (1) |
| Big Suamico, Suamico       | <0.01   | <0.01   | <0.01 (1) | <0.01 (1) |
| Fox River, Green Bay       | 0.18 <sup>b</sup> (3)   | 0.26    | 0.16      | 0.15      |

<sup>a</sup> Mean of two analyses unless noted otherwise.

<sup>b</sup> Fox River samples analyzed as Aroclor 1248. Late eluting components present near municipal waste treatment outfall.

Explicit chemical confirmations for the presence of PCBs in each sample were not possible in this study. PCBs with similar retention volumes and relative peak heights were confirmed in the fish from the Milwaukee River using i.r. and mass spectrometry (5). The analyses do not preclude the possible presence of other chemicals which may have similar chemical properties, such as the chloronaphthalenes.

The recoveries of PCBs from water samples which were "spiked" with Aroclor 1254 and 1260 were approximately 80 to 85 percent. Although the relative error at 1  $\mu\text{g/l}$  was about  $\pm 8$  percent, the relative error in replicate analyses of river waters at the 0.1  $\mu\text{g/l}$  level may increase to 15 to 20 percent.

## Results and Discussion

The results of the monitoring of five rivers in the Green Bay area for PCBs during 1971 are presented in Table 1. The concentration of PCBs in the Pensaukee and Big Suamico Rivers remained below the determinable limit of 0.01  $\mu\text{g/l}$  throughout the period of the study. The PCBs in the Peshtigo River below the city of Peshtigo were approximately 0.3 to 0.4  $\mu\text{g/l}$  (as Aroclor 1254) until May 21, 1971, but decreased to below the determinable limit by July 20, 1971. PCBs in the Oconto River below the city of Oconto were present at a concentration of 0.45  $\mu\text{g/l}$  (as Aroclor 1254) on December 29, 1970, but decreased during the spring of 1971 and were also below the determinable limit on the July 20 sampling date. In contrast, no trends in the concentrations of PCBs in the Fox River were observed, and the levels

were found to be above 0.1  $\mu\text{g/l}$  (as Aroclor 1248) throughout the study. It should be noted that the chromatograms of the PCB mixtures in the Oconto and Peshtigo Rivers were most similar to that of Aroclor 1254, whereas the mixtures in the Fox River were predominately Aroclor 1248, with minor components similar to those in Aroclor 1254 sometimes apparent.

The initial purpose in monitoring the tributaries of Green Bay was to relate the composition and concentration of PCBs in the major tributaries to those in the water from the Bay and to examine possible changes in the composition of PCBs in the sediments. The data obtained from the initial monitoring, which shows that the PCB concentrations in two of the major tributaries decreased sharply to below the determinable limit in 1971, suggests that the self-imposed restrictions on the sale of PCBs by Monsanto Company in 1970 and 1971 may be having an immediate effect in some river systems. Continued monitoring of the Fox River will be conducted to determine if the levels of PCBs arising from this highly industrial area will also diminish in the near future.

Although the analyses of water from Green Bay indicated the concentrations of PCBs varied from 0.07  $\mu\text{g/l}$  (as Aroclor 1248) at Long Tail Point near the city of Green Bay to 0.04  $\mu\text{g/l}$  approximately 35 miles northeast of the city near Sturgeon Bay, the variations introduced by windmixing and the inability to measure small concentration differences below the 0.05  $\mu\text{g/l}$  level may make it impossible to determine if the decline in PCBs in tributaries will be reflected in the water from the open Bay in the near future. Consequently,

the sampling program has been expanded to include fish and other organisms of the Bay which contain  $\mu\text{g/gm}$  quantities of the PCBs.

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